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Assistant Commissioner for Patents,
WASHINGTON, D.C. 20231,

ON November 11, 1999

Rupert B. Hurley Jr.

Rupert B. Hurley Jr.
Registration No. 29,313

November 11, 1999
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor: Childress et al

Attorney Docket No.: 41933-01

Serial No.: 08/354,177

Group Art Unit: 1761

Filing Date: 12/12/94

Examiner: Tran Lien

Title: HEAT SHRINKABLE FILMS CONTAINING SINGLE SITE
CATALYZED COPOLYMERS

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DECLARATION UNDER 37 CFR 1.132

Assistant Commissioner for Patents
Washington, D.C. 20231

State of South Carolina
County of Spartanburg

I, Blaine Childress, declare as follows:

1. That I received my Bachelor of Science Degree in Textile Chemistry at Auburn University in 1974; and received my Master of Science Degree in Textile Chemistry in 1978;

2. That from 1978 through April 1, 1998 I was employed by the Cryovac Division of W.R. Grace & Co.-Conn. in Duncan, South Carolina as Research Associate; that from April 1, 1998 to the present I have been employed by Cryovac, Inc. My career at Cryovac has included laboratory management including supervision of microscopy, thermal analysis, and spectroscopy. Since 1991 my focus has been in product development in the polymer science group of Research Development, and Engineering.

3. Exxon personnel visited the offices of the Cryovac Division of W.R. Grace & Co., to promote their new line of metallocene-catalyzed linear ethylene/alpha-olefin copolymers, which was a new homogeneous ethylene/alpha-olefin copolymer. These metallocene-catalyzed linear ethylene/alpha olefin resins supplied by Exxon have the same polymer architecture as the linear homogeneous ethylene/alpha olefin resins disclosed in U.S. Patent No. 3,645,992, to Elston ("ELSTON").¹ Exxon indicated these copolymers would be useful in preparing films. Exxon personnel stated that they had prepared blown films from their new metallocene-catalyzed linear homogeneous resins, and found these linear homogeneous resins to operate in a manner similar to linear low density polyethylene ("LLDPE"), but with clarity and strength improvements linked to single-site catalysis. The phrase "homogeneous resin" is synonymous with a resin produced with single site catalyst.

4. Thereafter, I began to examine the Exxon metallocene-catalyzed linear homogeneous ethylene/alpha-olefin copolymer resins for use in preparing heat shrinkable films in an effort to determine whether advantages seen by Exxon in evaluations in blown films could be could be seen in heat shrinkable films. I substituted the Exxon linear homogeneous resins for EVA resins, as well as for heterogeneous LLDPE, in a commercial film formulation using a commercial process. During my initial attempts to use the Exxon resin I quickly realized that the linear resin from Exxon did not operate like LLDPE when attempting to produce heat shrinkable films. For example, a 0.922 g/cc ethylene/hexene linear homogeneous resin from Exxon produced high extruder head

¹ See USPN 5,408,004, more particularly Column 3 lines 43-56.

pressure and low melt strength for all film structures attempted. Attempts to alleviate the high head pressure by raising the extruder temperature further weakened the polymer melt strength, and no quality heat-shrinkable film could be produced. Furthermore, slowing the process rate provided no relief to the problem. Much of the film did not survive the downward tape casting step, and that which did survive resulted in hazy, streaked film. I was surprised at this result due to the advertised excellent optical quality found by Exxon when making blown films and the statements made by Exxon personnel that these Exxon linear homogeneous resins behaved similarly to LLDPE when examined by their staff.

5. I discussed the extrusion performance of the Exxon resins with Mr. Gautam Shah, a Cryovac research and development colleague who had also investigated the performance of the Exxon linear homogeneous resins. Mr. Shah informed me that he too had experienced problems when attempting to extrude the homogeneous resins supplied by Exxon in structures wherein the Exxon resins were designed to serve as major components in a film. Moreover, Mr. Shah stated that the problems persisted even when the Exxon linear homogeneous resin was used in making an upward-blown film, (i.e., in a process quite different from the process used to make a heat-shrinkable film). Therefore, it was felt by both Mr. Shah and me that linear homogeneous resins such as discussed in ELSTON or supplied by Exxon were unsatisfactory for making heat shrinkable films. At this point it seemed clear to me that metallocene-catalyzed resins were not going to meet the initial expectations set by Exxon, and were unsuitable as replacements for LLDPE in preparing commercial heat shrinkable films.

6. Nevertheless, I continued to explore the potential of the new homogeneous resins. I attempted to prepare 2-ply films for use in our heat shrinkable patched bag at one of the U.S. Cryovac factories. Although I continued to experience the undesirable high extruder head pressure, I produced good quality 2-ply film wherein the linear metallocene-catalyzed Exxon resin replaced the ethylene/vinyl acetate (EVA) copolymer within the second layer of a commercial heat shrinkable patch film formulation otherwise in accordance with U.S. Patent No. 4,770,731, to Ferguson ("FERGUSON"). The second

layer of the commercial heat shrinkable patch film made up only 15% of the total film thickness. [See Exhibit F.] Next, I produced good quality film by further replacing the EVA component of the blended first layer of the film. This first layer makes up 85% of the film thickness and is formulated with a blend of 10% EVA, 87% LLDPE and 3% LDPE. Thus, a film could be produced having both EVAs replaced by the Exxon metallocene catalyzed linear homogeneous resin comprising about 23.5% the film structure. [See Exhibit G.]

7. However, when attempts were made to use the linear homogeneous resin to replace the LLDPE component of the commercial heat shrinkable patch in accordance with FERGUSON, no film could be produced. A blend of 10% EVA, 3% antiblock, and 87% of the Exxon linear homogeneous resin in the first layer of the film, did not provide sufficient melt strength to produce the heat shrinkable patch film. The melt strength was unsatisfactory despite slowing the process significantly and lowering the extrusion temperature. [See Exhibit H.] Attempts to salvage the factory experiment by increasing the EVA content of the thicker first layer of the heat shrinkable patch film beyond the level of that of the film of FERGUSON also met with unsatisfactory operability. [See Exhibit J.] Thus, while heat shrinkable films comprising linear homogeneous resins could be produced as modifications to the film formulations taught by FERGUSON, those modifications were limited to designs in which the loading of linear homogeneous ethylene/alpha olefin resin within the film construction did not exceed about 85%. Again, it seemed clear that Exxon's statements regarding their experience in blown films with their new linear homogeneous resins could not be generally applied to the commercial manufacture of heat shrinkable films such as for patch, especially with regard to replacing LLDPE. Indeed, testing with other linear homogeneous resins, wherein the linear homogeneous resin replaced all of the LLDPE as well as all of the EVA in the first layer of the heat-shrinkable patch film, resulted in complete failure. [See Exhibit K.] More particularly, when the resins forming both the first and second layers of the heat shrinkable patch film disclosed in FERGUSON were replaced almost entirely with linear homogeneous resins from Exxon, no film could be produced. [See Exhibit L.] Thus, one of ordinary skill in the art

would have to conduct undue experimentation to determine whether linear homogeneous resins such as those from Exxon *could* be used as replacements for the resins of the heat shrinkable patch films, i.e., as a substitute for the LLDPE in the heat shrinkable patch of FERGUSON. [Again, see Exhibit H, which demonstrates that Exxon linear homogeneous resins are not a suitable "drop-in" for 87% LLDPE when attempting to produce the heat shrinkable patch film formulation of FERGUSON.]

8. After many unsuccessful attempts at using Exxon linear homogeneous resin to produce heat shrinkable films on commercial equipment, I discovered that adding another selected resin, such as high density polyethylene, to a linear homogeneous resin, for instance in an amount of about 15%, could be used to reinforce the melt strength of the deficient linear homogeneous resin, and could allow me to produce heat shrinkable films using linear homogeneous resin. Similarly, I discovered that I could blend 30% low density polyethylene with 70% Exxon linear homogeneous resin to successfully produce heat shrinkable film on commercial equipment. At levels of about 85% of linear homogeneous resin, a reinforcing polymer is required to provide adequate melt strength to the film using the commercial process for making heat shrinkable films, especially those for use as a heat shrinkable patch. In addition to blending with reinforcing materials (materials such as HDPE, LLDPE, LDPE, EVA, etc.), I discovered yet additional ways to repair the deficiencies of linear homogeneous resins, such as the Exxon metallocene catalyzed resin. For example, I could add additional layers to a heat shrinkable patch film construction, and thereby place the melt strength donating material within separate layers to support the film melt curtain during the commercial downward casting step. With such a reinforcing strategy, I was able to make heat shrinkable films comprising linear homogeneous resin in amounts up to about as high as 85%, based on total film weight, using the commercial manufacturing method as otherwise disclosed in FERGUSON. Of course, the need for such reinforcement by blending or multilayer construction was not taught by the disclosure of ELSTON, or by Exxon when discussing blown films, but instead was learned through extensive experimentation.

9. I learned that I could also select a different process than taught by FERGUSON to produce heat shrinkable patch films having high levels of the linear homogeneous resin. For instance, I could extrude film using a flat cast process rather than the downward cast process of FERGUSON, thereby avoiding the melt strength issues associated with the Exxon linear homogeneous resins by way of mechanical support from the casting roller. Surprisingly, if extruding using a horizontal slot die, I could successfully produce a film comprising 100% Exxon linear homogeneous resin, then collect the roll of thick film for solid state orientation using a tenter frame process. However, I reiterate that substitution of the LLDPE component of FERGUSON with a linear homogeneous resin, such as disclosed by ELSTON or supplied by Exxon, is inoperable in the film and process of FERGUSON.

10. The following Table provides a summary of some of my inventive activity discussed above. Note that operability was "YES" for the Control (film of FERGUSON, i.e., Exhibit E), as well as when I used the linear homogeneous copolymer at levels of about 15% and 23½% of the total patch film structure. On the other hand, operability was "MARGINAL" at 82% linear homogeneous copolymer, and operability was "NO" with the highest loadings of linear homogeneous copolymer in the modification to commercial patch film structure using the commercial manufacturing process.

Exhibit	Notebook Page	Operability	Comment
E [Control*]	239360	YES	Control B003 successfully made (87%LLDPE in First Layer)
F	239361	YES	SLP 4008 (0.885 g/cc, 4.0 MI E/H resin) replacing EVA Layer (15% of film structure)

G	239362	YES	SLP 4008 replacing Second Layer; SLP 3011D (0.900 g/cc, 1.0 MI E/H resin) replacing EVA component of First Layer (23½% of total film structure)
H	240416	NO	87% Exxon SLP 402G (0.917 g/cc, 1.1MI, ethylene/hexene resin) in First Layer
J	240414	MARGINAL	82% Exxon SLP 404H (0.928 g/cc, 0.83MI, E/H resin) in First Layer (made with difficulty)
K	240415	NO	First Embodiment: 97% Exxon SLP 402G in First Layer Second Embodiment: 97% Exxon SLP 404H in First Layer
L	239363	NO	SLP 9017 (0.920g/cc, 3.0 MI, ethylene/hexene resin) replacing LLDPE and EVA in First Layer; SLP 4008 replacing EVA in Second Layer

* Film made according to FERGUSON

11. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Further Declarant sayeth not.

Blaine C Childress

Blaine C. Childress

PROBLEM NO.

137-017

DATE

CRYOVAC

SUBJECT: B003 Alternate RESINS

This project is a replacement resin for the seal layer. During transition the optics of the bubble became much worse. Also the head pressure and amps increased significantly.

EXHIBIT

F

Extruder & Die Conditions

RDT Conditions

Cold Bath Conditions

Loop 1

"B"

"C"

Die

Beam 1

21.0

Shoe Size

15.5

1-200/150

470/125

377/400

Beam 2

20.3

Shoe Length

15"

2-200/270

405/125

417/400

K V

500

Shoe/Die Dist.

5"

3-205/315

405/125

483/450

Inv. Pos

75

Seal Air

80 S.F.F.

4-313/320

373/370

505/410

Varinc

85

Water Ring Sec

15

5-302/325

374/370

475/400

Water Flow

35 -P/M

6-314/325

410/410

475/400

Water Temp

42°F

Melt Temp: 345

483

Inv. Pos.

Head Press: 7500

(330)

Varinc

9

RPM: 1425

76.6

Dust Type

Macro MARK 20

Amps: 12.4

36.7

Duster Set

16

Driven Roll Speeds

Recking Conditions

Cold Bath 41.1

Steam 213/213

Dust Main Air 70

Inrad In 41.7

EG Air 260/260

Dust Stem Air 28

Inrad Out 41.5

Vertical Air 295/296 Auto

Dust Vibration 42

Inv. Exit 41.2

Tape Temp 233/234

Line rate was decreased to accommodate the increased head pressure.

Oven 41.6

Film Temp 181/180

Oven Exit 45.8

Air Ring % 67.2

Deflate 154.4

Vert. Den. Sig 1.5

Teg. W. p. 136.6

Footage 1000

ca./deflate

Taper 1

Long R.R. 3.75

Tension 40

Trans R.R.

Tape Gr. 29.1 Tape Width 15 1/4

A/B/B/ Structure

Film Gr. 4.50 Film Width 56

A: 81.02 LLDPE B: Exxon Exact SLP400B

10.0% EVA

Lot # 90201

3.0% Additive Package

CONFIDENTIAL

SIGNED

UNDERSTOOD AND WITNESSED:

DATE

DATE

No 239361 B

PROBLEM NO. 137-017 DATE

CRYOVAC

SUBJECT: 3003 Alternate Resins

This project is a replacement for EVA which is one of the three components of the outer layer. The replacement resin will be EXXON EXACT SLP 3011D

EXHIBIT

lot No. 90246. The optics are still poor. NOT ANY better than the standard film.

Extruder and Die Conditions

RDI Conditions

Racking Conditions

	"B"	"C"	Die
Loop #1	250/320	437/415	400/400
2	270/320	425/425	420/400
3	322/315	425/425	430/400
4	313/320	374/375	510/400
5	321/325	371/375	475/405
6	312/325	411/400	477/475

Beam 1	20.5
Beam 2	20.3
KV	500
Inv. Pos	
Variac	85

Steam	213/343
E.Q. Air	260/300
Vert. Air	312
Tape Temp	181/180
Film Temp	181/180
Air Ring %	71
Vert. Oven Slope	1.50

Melt Temp.	249
Feed Press.	7500
R.P.M.	14.5
Amps	181

Shoe Size	15.5
Shoe Length	15"
Shoe/Die Dist.	5"
Shoe A.W.	80
Water Ring Size	15"
Water Flow	35
Water Temp.	42
Inv. Pos	
Variac	9
Duster Set	16
Main Air	68
Steam Air	78
Vibrator	42
Line Spd Ref.	82.7

Taper	1
Tension	40
Footage	8600

Driven Roll Speed	
Cold Bath	42.8
Inrad. IN	43.5
Inrad. Out	43.2
Inv. Exit	44.3
Oven	43.7
Oven Exit	45.4
Debate	158.4
ISO Nips	147.7

Long. Racking Ratio	3.72
Trans. Racking Ratio	

Tape Ga. 29 Tape Width 15 1/2
Film GA 450 Film Width 56

A/B//B/A Structure

A = 87.0% LLDPE (lot #90246) B = Exxon Exact SLP 3011D
10.0% Exxon Exact (SLP 3011D)
3.0%

CONFIDENTIAL

SIGNED *James H. [Signature]*
DATE

UNDERSTOOD AND
WITNESSED:
DATE

By [Signature]

No 239362

PROBLEM NO.

DATE:

SUBJECT: LINE 01 IOWA PARK BOOZ ALT. RBWS

CRYOVAC

⑤ REPLACE LLOPE WITH SLP 402 G

EXHIBIT:

H.

87% SLP 402 G

10% EVA

3% additive package

CONDITIONS SAME AS CONTROL NBR 240413

EXT B HP - 5500
MT -
AMPS -
RPM -

EXT C HP -
MT -
AMPS -
RPM -

ZONE 1 - 380
2 - 380
3 - 380
4 - 380

GATE - 380
ADAPTER - 380

COLD BATH -
OVEN -
EXIT -
DEFATE -
ISULATION -

OVEN STEAM -
H₀ -
V₀ -

TAPE TEMP -
FILM TEMP -

RDI
SPEED REF. -
IN -
EXIT -

SEAM 1 -
2 - 7 TOTAL

LOW MELT STRENGTH - COULD NOT KEEP
TAPE FROM PILING UP ON SHOE - TRIED LOWER
EXTRUDER TEMP PROFILE - SEE ABOVE.

⑥ INCREASE % EVA

82% SLP 402 G

5% EVA

3% Additive Package

SAME PROBLEM AS #5 ABOVE

CONFIDENTIAL

SIGNED

UNDERSTOOD AND
WITNESSED:

DATE

DATE

NS 240416 B

PROBLEM NO.

DATE

SUBJECT: LINE 01 IOWA PARK 6002 ALT. RESINS TRIALS

CRYOVAC

② REDUCE LLDPE^W/SLP 404H

EXHIBIT

J

BLEND - 82% SLP 404H (0.83 MI)

15% EVA

3% Additive Package

LOWERED LINE SPEED REF. TO 68.8 (40.2 FPM COLD BATH)
ON STANDARD MAT'L BEFORE CHANGE OVER - THIS LOWERED
EXT C HEAD PRESSURE TO 5500 PSI

ALL CONDITIONS SAME AS CONTROL EXCEPT:

EXT B HP - 4600
MT - 257
AMPS - 115
RPM - 12.2

EXT C HP - 7300
MT - 489
AMPS - 359
RPM - 57.0

COLD BATH - 40.3

OVEN - 41.3

EXIT - 47.1

DEWATE - 166

ISOLATION - 150

OVEN STEM - 215

HO - 270

VO - 278

TAPE TEMP - 240

FILM TEMP - 179

ROI

SPEED REF - 68.8

DM - 40.6

EXIT - 41.0

BEAM 1 - 24.0

2 - 23.9

6.0 MI

47.4
TOTAL

RATIOS - MD 166/40.3 4.1

TD 525/15.2 3.4

TOTAL 13.94

BUBBLE BROKE AFTER

2020 FT. STABILITY

NOT GREAT - PROBABLY

CAUSED BY FOLD IN TAPE -

TIME FOR HEAT SEAL -

SHRINK 11% x 12% TEST 1
11% x 14% TEST 2

CONFIDENTIAL

SIGNED

UNDERSTOOD AND
WITNESSED:

DATE

DATE

Blaine Children

No 240414

B

PROBLEM NO. 122-00

DATE

SUBJECT: LIVE 01 IOWA PARK 8002 ALT RESIN TRIALS

CRYOVAC

(3) REPLACE LLOPE and EVA WITH SLP 404 H

EXHIBIT

97% SLP 404 H (0.83 MI)

3% Additive PKG

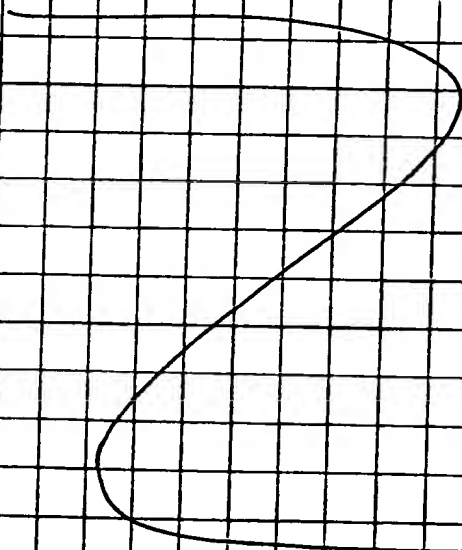
TAPE KEPT PILING UP ON SHOE - UNABLE TO RESTART LINE
BEFORE RUNNING OUT OF SLP 404 H.

(4) REPLACE LLOPE AND EVA WITH SLP 402 G

97% SLP 404 G (1.11 MI)

3% Additive PKG

DID NOT ATTEMPT - WOULD NOT RUN WITH
10% EVA - SEE NBPN 240416



CONFIDENTIAL

SIGNED

[Signature]

UNDERSTOOD AND
WITNESSED:

Alaine Childress

DATE

DATE

No 240415 B

PROBLEM NO. 131 JOIT

DATE July 16, 1972

1972

SUBJECT: 3003 Alternate Resins

This project is a replacement for LLOPE. LLOPE is the base resin for the outer layer blend. The replacement resin will be Exxon Exact JOIT lot # 90239

EXHIBIT

A

Extruder & Die Conditions

ADI conditions

Reeling Conditions

Loop #

1

2

3

4

5

6

Melt Temp

Head Press.

R.P.M.

Amperes

Driven Roll Speeds

Colet Bath

Inner Tow

Inner Out

Inner Roll

Oven

Oven Ent

Definitor

Top Wips

EB/DeRate

Long R.R.

Trans R.R.

Tape Gr.

Film Gr.

39

Tape Width

Film Width

54

A/B/A/A Structure

A/B/A/A Structure

A/B/A/A Structure

A/B/A/A Structure

EXXON EXACT SUP 9017

EXXON EXACT SUP 9017

EXXON EXACT SUP 9017

EXXON EXACT SUP 9017

EXXON EXACT SUP 9017

EXXON EXACT SUP 9017

EXXON EXACT SUP 9017

No conditions were taken due to time limitations. We couldn't get the resin extruder and anograph. SUP 9017 will be explored further at a later date.

Additive PHA

7/16-72

7/16-72

CONFIDENTIAL

SIGNED

DATE

James H. Walker III
July 16, 1972

UNDERSTOOD AND
WITNESSED

DATE

John D. Smith III

No 239363 B